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ON THE PROJECTIVE AND EQUI-PROJECTIVE GEOMETRIES OF PATHS

By Tracy Yerkes Thomas*

Zürich, Switzerland

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1. *Projective Geometry of Paths.*—(Cf. H. Weyl, *Göttingen Nachrichten*, 1921, p. 99; also O. Veblen and T. Y. Thomas, *Trans. Amer. Math. Soc.*, **25**, 1923, p. 551.) In a sense the projective geometry of paths is the *true geometry of paths* for we are here concerned with properties of the paths apart from their definition by means of a particular affine connection $\Gamma^i_{\alpha\beta}$. When the affine connection $\Gamma^i_{\alpha\beta}$ of an affine geometry of paths is replaced by an affine connection $\Lambda^i_{\alpha\beta}$ in accordance with the equations

$$\Lambda^i_{\alpha\beta} = \Gamma^i_{\alpha\beta} + \delta^i_\alpha \Phi_\beta + \delta^i_\beta \Phi_\alpha \qquad (1.1)$$

where Φ_α is an arbitrary covariant vector, the set of functions $\Lambda^i_{\alpha\beta}$ defines the same system of paths as the set of functions $\Gamma^i_{\alpha\beta}$. Also any two sets of functions $\Gamma^i_{\alpha\beta}$ and $\Lambda^i_{\alpha\beta}$ defining the same system of paths are related by equations of the form (1.1).

2. *The Projective Connection.*—One of the problems of the projective geometry of paths is the problem of the projective equivalence of two affine spaces of paths, i.e., the problem of the determination of the conditions under which there exists a transformation.

$$x^i = \varphi^i(\bar{x}^1, \bar{x}^2, \ldots, \bar{x}^n), \quad \Delta = \left|\frac{\partial x}{\partial \bar{x}}\right| \neq 0 \qquad (2.1)$$

mapping two affine spaces of paths upon one another in such a way that the paths of one space are mapped upon the paths of the other. Let us denote the affine connection of two affine spaces of paths by sets of functions $\Gamma^i_{\alpha\beta}$ and $\bar{\Gamma}^i_{\alpha\beta}$, respectively. We then have that a necessary and sufficient condition for the projective equivalence of the two spaces is that there exists a relation (2.1) and vector Φ_α which satisfy the equations

$$\Gamma^i_{\alpha\beta} + \delta^i_\alpha \Phi_\beta + \delta^i_\beta \Phi_\alpha = \frac{\partial x^i}{\partial \bar{x}^\gamma}\left(\frac{\partial^2 \bar{x}^\gamma}{\partial x^\alpha \partial x^\beta} + \bar{\Gamma}^\gamma_{\mu\nu}\frac{\partial \bar{x}^\mu}{\partial x^\alpha}\frac{\partial \bar{x}^\nu}{\partial x^\beta}\right). \qquad (2.2)$$

Eliminating the vector Φ_α from the equations (2.2) we have

$$\bar{\Pi}^{\sigma}_{\alpha\beta}\frac{\partial x^i}{\partial \bar{x}^\sigma} = \Pi^i_{\sigma\tau}\frac{\partial x^\sigma}{\partial \bar{x}^\alpha}\frac{\partial x^\tau}{\partial \bar{x}^\beta} + \frac{\partial^2 x^i}{\partial \bar{x}^\alpha \partial \bar{x}^\beta} - \frac{1}{n+1}\frac{\partial \log \Delta}{\partial \bar{x}^\alpha}\frac{\partial x^i}{\partial \bar{x}^\beta} - \frac{1}{n+1}\frac{\partial \log \Delta}{\partial \bar{x}^\beta}\frac{\partial x^i}{\partial \bar{x}^\alpha}, \quad (2.3)$$

where

$$\Pi^i_{\alpha\beta} = \Gamma^i_{\alpha\beta} - \frac{\delta^i_\alpha}{n+1}\Gamma^\sigma_{\sigma\beta} - \frac{\delta^i_\beta}{n+1}\Gamma^\sigma_{\sigma\alpha}. \quad (2.4)$$

The functions $\bar{\Pi}^i_{\alpha\beta}$ have a similar definition in terms of the affine connection $\bar{\Gamma}^i_{\alpha\beta}$. These functions are independent of the particular affine connection by means of which the paths are defined, and constitute a normalized affine connection which I shall speak of as the *projective connection* $\Pi^i_{\alpha\beta}$. We observe that

$$\Pi^\sigma_{\sigma i} = 0 \quad (2.5)$$

identically.

3. *The Projective Parameter.*—The set of differential equations

$$\frac{d^2x^i}{dp^2} + \Pi^i_{\alpha\beta}\frac{dx^\alpha}{dp}\frac{dx^\beta}{dp} = 0 \quad (3.1)$$

defines our system of paths. Also any set of differential equations of the paths may be put into the form (3.1) for a proper choice of the parameter p. The parameter p is thus a normalized parameter which is independent of the particular set of functions $\Gamma^i_{\alpha\beta}$ defining the paths and which I shall call the *projective parameter* p.

Under the arbitrary transformation (2.1) the projective parameter p becomes $\bar{p}$, and there exists a relation

$$p = f(\bar{p}) \quad (3.2)$$

between the parameters p and $\bar{p}$ along any particular path. In general the relation (3.2) will depend on the particular path and may contain certain arbitrary constants expressing the indeterminateness of the parameters. We shall wish to find the explicit form of the relation (3.2).

With little difficulty we may show that

$$\frac{\left[\bar{\Pi}^i_{\sigma\tau} - \left(\Pi^\lambda_{\alpha\beta}\frac{\partial x^\alpha}{\partial \bar{x}^\sigma}\frac{\partial x^\beta}{\partial \bar{x}^\tau} + \frac{\partial^2 x^\lambda}{\partial \bar{x}^\sigma \partial \bar{x}^\tau}\right)\frac{\partial \bar{x}^i}{\partial x^\lambda}\right]\frac{d\bar{x}^\sigma}{d\bar{p}}\frac{d\bar{x}^\tau}{d\bar{p}}}{\frac{d\bar{x}^i}{d\bar{p}}} = \frac{\frac{d^2\bar{p}}{dp^2}}{\left(\frac{d\bar{p}}{dp}\right)^2}, \quad (3.3)$$

in which we know that the bracket

$$\bar{\Pi}^i_{\sigma\tau} - \left(\Pi^\lambda_{\alpha\beta}\frac{\partial x^\alpha}{\partial \bar{x}^\sigma}\frac{\partial x^\beta}{\partial \bar{x}^\tau} + \frac{\partial^2 x^\lambda}{\partial \bar{x}^\sigma \partial \bar{x}^\tau}\right)\frac{\partial \bar{x}^i}{\partial x^\lambda}$$
$$= \delta^i_\sigma \Phi_\tau + \delta^i_\tau \Phi_\sigma \qquad (3.4)$$

for some vector Φ_σ. Putting $i = \tau$ in (3.4) we have

$$(n+1)\Phi_\sigma = -\frac{\partial}{\partial \bar{x}^\sigma}\log \Delta. \qquad (3.5)$$

Also we easily find

$$2\Phi_\sigma \frac{\partial \bar{x}^\sigma}{\partial x^\tau}\frac{d\bar{x}^\tau}{dp} = \frac{d}{dp}\log\left(\frac{d\bar{p}}{dp}\right). \qquad (3.6)$$

The equations (3.5) and (3.6) now give

$$\frac{dp}{d\bar{p}} = \Delta^N, \qquad N = 2/(n+1) \qquad (3.7)$$

the constant of integration being absorbable into the parameters. In (3.7) Δ is to be regarded as a function of $\bar{p}$ obtained by eliminating the variables $(\bar{x})$ occurring in Δ by means of the parametric equations of the path. Integrating (3.7) with the initial condition $p = 0$ when $\bar{p} = 0$ we have

$$p = \int_0^{\bar{p}} \Delta^N(\bar{p})d\bar{p} \qquad (3.8)$$

as the explicit form of (3.2).

4. *Equivalence Theorem for the Projective Geometry of Paths.*—Purely analytically the problem of the projective equivalence of two affine spaces is simply the problem of the determination of the integrability conditions of the equations (2.3). The determination of these integrability conditions in satisfactory form appears to me to be the *fundamental problem of the projective geometry of paths*. Comparison with the affine case would lead us to expect that if algebraic conditions of integrability are attainable that we shall have in these conditions the analytic material for the development of the projective geometry of paths corresponding to the development of the affine geometry of paths. But the solution of this problem remains for the present open.

5. *Equi-Projective Geometry of Paths.*—Let us now consider those transformations (2.1) which satisfy the condition

$$\Delta = 1 \qquad (5.1)$$

Geometrically this means that we shall consider transformations leaving volume unchanged. Thus the set of vectors $\xi^i_{(\alpha)}$ ($i, \alpha = 1, 2, \ldots, n$) define the volume $|\xi^i_{(\alpha)}|$ and this volume is invariant under transformations satisfying (5.1). As there seems to be no single word in the English language descriptive of this class of transformations I shall here take the liberty of introducing the word *equi-transformation* for an arbitrary transformation (2.1) satisfying (5.1). We shall also find it convenient to speak of *equi-projective* properties of the paths as those properties independent of any particular affine connection $\Gamma^i_{\alpha\beta}$ which are invariant under equi-transformations. The body of theorems expressing equi-projective properties of the paths will constitute the *equi-projective geometry of paths*. (It is also clear what would be meant by the *equi-affine geometry of paths*. We may note that the word "equi-affine" which here appears does not have the same meaning as the word "equiaffine" used by O. Veblen, these PROCEEDINGS, **9** 1923, p. 3.)

For the equi-projective geometry of paths the equations (2.3) become

$$\bar{\Pi}^\sigma_{\alpha\beta} \frac{\partial x^i}{\partial \bar{x}^\sigma} = \Pi^i_{\sigma\tau} \frac{\partial x^\sigma}{\partial \bar{x}^\alpha} \frac{\partial x^\tau}{\partial \bar{x}^\beta} + \frac{\partial^2 x^i}{\partial \bar{x}^\alpha \partial \bar{x}^\beta}. \tag{5.2}$$

The equations of transformation on the projective connection $\pi^i_{\alpha\beta}$ in the equi-projective geometry of paths have therefore the same form as the equations of transformation of the affine connection $\Gamma^i_{\alpha\beta}$ in the affine geometry of paths. Also (3.8) gives

$$p = \bar{p}, \tag{5.3}$$

for the equi-projective geometry of paths.

6. *Equi-Projective Normal Coördinates.*—Normal coördinates may be erected for the equi-projective geometry of paths in the same manner as for the affine geometry of paths. Thus the equations (3.1) possesses a unique solution of the form

$$x^i = q^i + \Gamma^i(q, \xi p) \tag{6.1}$$

(Cf. O. Veblen and T. Y. Thomas, *Trans. Amer. Math. Soc.*, **25**, 1923, p. 551) which satisfies a set of initial conditions

$$x^i = q^i \text{ when } p = 0; \frac{dx^i}{dp} = \xi^i \text{ when } p = 0. \tag{6.2}$$

Introducing the substitution

$$z^i = \xi^i p \tag{6.3}$$

into the equations (6.1) these equations become

$$x^i = q^i + \Gamma^i(q, z) \tag{6.4}$$

and define a set of *equi-projective normal coördinates* (z). The equations of a path passing through the origin of the equi-projective normal coördinate system (z) are given by (6.3). Under an arbitrary equi-transformation (2.1) of the general (x) coördinates, the equi-projective normal coordinates (z) which are defined by the (x) coördinates and a point (q) suffer a transformation of the form.

$$z^i = a^i_\alpha \bar{z}^\alpha \tag{6.5}$$

where the a's are constants such that

$$a^i_\alpha = \left(\frac{\partial x^i}{\partial \bar{x}^\alpha}\right)_q \tag{6.6}$$

evaluated at the point (q). It follows from (6.6) that (6.5) is an equi-transformation. We have also that

$$\left|\frac{\partial x}{\partial z}\right| = \left|\frac{\partial \bar{x}}{\partial \bar{z}}\right| \tag{6.7}$$

for the equi-projective geometry of paths.

7. *Equi-Tensors and Equi-Projective Extension.*—By an *equi-tensor* will be meant a set of quantities $T^{lm\ldots n}_{ij\ldots k}$ $(i, j, \ldots, k, l, m, \ldots, n = 1, 2, \ldots, n)$ which transforms as an ordinary tensor under equi-transformations. We immediately see that the ordinary process of extension applied to a tensor or equi-tensor but with the projective connection $\Pi^i_{\alpha\beta}$ replacing the affine connection $\Gamma^i_{\alpha\beta}$ gives rise to an equi-tensor of higher order. This proces of extension involving the projective connection $\Pi^i_{\alpha\beta}$ will be called *equi-projective extension.*

8. *Equi-Projective Normal Tensors and the Equi-Projective Curvature Tensor.*—By replacing the affine connection $\Gamma^i_{\alpha\beta}$ in the expressions for the ordinary normal tensors by the projective connection $\Pi^i_{\alpha\beta}$ we obtain the equi-projective normal tensors which I shall denote by $\mathfrak{A}^i_{\alpha\beta\gamma\ldots\tau}$. In a similar manner we obtain the equi-projective curvature tensor $\mathfrak{B}^i_{\alpha\beta\gamma}$.

I express my thanks to Prof. H. Weyl with whom I have spoken of the results in this paper and who has kindly read it through.

* NATIONAL RESEARCH FELLOW IN MATHEMATICAL PHYSICS.

PROJECTIVE NORMAL COÖRDINATES FOR THE GEOMETRY OF PATHS

BY OSWALD VEBLEN AND JOSEPH MILLER THOMAS*

PRINCETON UNIVERSITY

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1. The purpose of this note is to introduce into the geometry of paths a system of coördinates which are determined in an invariant fashion by the paths themselves, and are independent of the components of affine connection which appear in the differential equations of the paths. They are therefore suitable for the determination of projective invariants in a manner analogous to the determination of affine invariants by means of affine normal coördinates.[1] They are like affine normal coördinates in that the equations of the paths through the origin are linear in terms of them, and also in that they are related to the arbitrary system of coördinates from which they arise by a tangential condition. But they also have the property that the ratio of the products of the differentials in the special and general coördinate systems is stationary at the origin.

2. The paths are solutions of the differential equations

$$\frac{d^2x^i}{ds^2} + \Gamma^i_{jk}\frac{dx^j}{ds}\frac{dx^k}{ds} = 0, \tag{2.1}$$

and also of the system obtained by replacing the components Γ^i_{jk} of the affine connection by

$$\Gamma^i_{jk} + \delta^i_j\,\phi_k + \delta^i_k\,\phi_j,$$

where ϕ_j are the components of an arbitrary vector. The quantities[2]

$$\Pi^i_{jk} = \Gamma^i_{jk} - \frac{\delta^i_j}{n+1}\Gamma^\alpha_{\alpha k} - \frac{\delta^i_k}{n+1}\Gamma^\alpha_{\alpha j}$$

have the same value for all affine connections and may be called the *components of the projective connection.*

If the Π's in another coördinate system y are denoted by P's we have

$$P^i_{\alpha\beta}\frac{\partial y^\alpha}{\partial x^j}\frac{\partial y^\beta}{\partial x^k} = \Pi^\alpha_{jk}\frac{\partial y^i}{\partial x^\alpha} - \frac{\partial^2 y^i}{\partial x^j \partial x^k} + \frac{\partial y^i}{\partial x^j}\frac{\partial \theta}{\partial x^k} + \frac{\partial y^i}{\partial x^k}\frac{\partial \theta}{\partial x^j}, \tag{2.2}$$

where

$$\theta = \frac{\log\,\Delta(y, x)}{n+1}, \tag{2.3}$$

and $\Delta(y, x)$ is the jacobian $|\partial y^i/\partial x^j|$. In terms of a new parameter defined by

$$t = \int e^{-\frac{2}{n+1}\int G^\alpha_{\alpha\beta}\, dy^\beta}\, ds, \tag{2.4}$$

where the G's denote the components of the Γ's in the y coördinate system and the integrals are evaluated along the path in question, the equations of the paths can be written

$$\frac{d^2y^i}{dt^2} + P^i_{jk}\frac{dy^j}{dt}\frac{dy^k}{dt} = 0. \tag{2.5}$$

A necessary and sufficient condition that the paths through the origin $y^i = 0$ be given by

$$y^i = \eta^i t,$$

where η^i are constants, is that

$$P^i_{jk}\, y^j\, y^k = 0 \tag{2.6}$$

be identically satisfied. By substitution in (2.6) from (2.2) we find that the differential equations for determining the y's as functions of the x's are

$$\left(\Pi^\alpha_{\beta\gamma}\frac{\partial y^i}{\partial x^\alpha} - \frac{\partial^2 y^i}{\partial x^\beta \partial x^\gamma} + \frac{\partial y^i}{\partial x^\beta}\frac{\partial \theta}{\partial x^\gamma} + \frac{\partial y^i}{\partial x^\gamma}\frac{\partial \theta}{\partial x^\beta}\right)\frac{\partial x^\beta}{\partial y^j}\frac{\partial x^\gamma}{\partial y^k}\, y^j\, y^k = 0. \tag{2.7}$$

By repeated differentiation of these equations, we can show that they possess a unique system of solutions satisfying the initial conditions

$$y^i = 0, \quad \frac{\partial y^i}{\partial x^j} = p^i_j, \quad \frac{\partial \theta}{\partial x^i} = p_i, \quad \text{for } x^i = q^i,$$

where p^i_j and p_i are any constants such that $|p^i_j| \neq 0$.

The coördinates y determined so as to satisfy (2.7) and the initial conditions

$$y^i = 0, \quad \frac{\partial y^i}{\partial x^j} = \delta^i_j, \quad \frac{\partial \theta}{\partial x^i} = 0, \quad \text{for } x^i = q^i, \tag{2.8}$$

will be called the *projective normal coördinates* associated with the coördinate system x and the point $x = q$. Direct calculation shows the invariant character of these coördinates, that is, if the projective normal coördinates associated with any coördinate system $\bar{x}$ and the same point be de-

noted by $\bar{y}$, they will satisfy the same equations (2.7) as the y's. In particular, we have that the $\bar{y}$'s satisfy

$$\left[P^{\alpha}_{\beta\gamma}\frac{\partial\bar{y}^i}{\partial y^{\alpha}}-\frac{\partial^2\bar{y}^i}{\partial y^{\beta}\partial y^{\gamma}}+\frac{\partial\bar{y}^i}{\partial y^{\beta}}\frac{\partial\theta(\bar{y},y)}{\partial y^{\gamma}}+\frac{\partial\bar{y}^i}{\partial y^{\gamma}}\frac{\partial\theta(\bar{y},y)}{\partial y^{\beta}}\right]\frac{\partial y^{\beta}}{\partial\bar{y}^j}\frac{\partial y^{\gamma}}{\partial\bar{y}^k}\bar{y}^j\bar{y}^k=0. \quad (2.9)$$

Moreover it follows from (2.8) and the multiplication theorem for jacobians that the initial values for $\bar{y}^i$ as solutions of (2.9) are

$$\bar{y}^i=0, \quad \frac{\partial\bar{y}^i}{\partial y^j}=b^i_j, \quad \frac{\partial\theta(\bar{y},y)}{\partial y^j}=a_j, \quad \text{for } y^i=0, \quad (2.10)$$

where

$$b^i_j=\left(\frac{\partial\bar{x}^i}{\partial x^j}\right)_q, \qquad a_j=\left[\frac{\partial\theta(x,\bar{x})}{\partial x^j}\right]_q, \quad (2.11)$$

the subscript q denoting evaluation for $x=q$.

By substitution it is readily verified that the functions

$$\bar{y}^i=\frac{b^i_{\alpha}\,y^{\alpha}}{1+a_{\alpha}\,y^{\alpha}} \quad (2.12)$$

satisfy (2.9) and (2.10). As seen above, there is a unique solution of (2.9) satisfying the initial conditions (2.10) Hence we have the

THEOREM.—*When the coördinates x undergo an arbitrary analytic transformation, the projective normal coördinates associated with the coördinate system x and a point $x=q$ undergo a linear fractional transformation.*

3. In order to apply the coördinates defined above to the problem of finding projective tensors, we note that from (2.6) follows

$$(P^i_{jk})_0=0.$$

Hence we can write

$$P^i_{jk}=Q^i_{jkl}\,y^l+\tfrac{1}{2}\,Q^i_{jkl\phi}\,y^l\,y^{\phi}+\ldots, \quad (3.1)$$

with a similar expression for the barred quantities. From (2.12) and (2.2) we have

$$P^{\alpha}_{jk}\frac{\partial\bar{y}^i}{\partial y^{\alpha}}=\bar{P}^i_{\alpha\beta}\frac{\partial\bar{y}^{\alpha}}{\partial y^j}\frac{\partial\bar{y}^{\beta}}{\partial y^k}. \quad (3.2)$$

Substituting from

$$\frac{\partial\bar{y}^i}{\partial y^j}=\left(\frac{\partial\bar{x}^i}{\partial x^j}\right)_q+\left(\frac{\partial^2\bar{y}^i}{\partial y^j\partial y^{\alpha}}\right)_0 y^{\alpha}+\ldots$$

and from (2.12) and (3.1) in (3.2), we find on equating coefficients of y^l that the functions Q^i_{jkl} are the components of a tensor which, being defined in projective coördinates, is independent of the choice of the affine connection.

Differentiation of (2.2) and evaluation at $y^i = 0$ by means of (2.7) and (2.8) give

$$Q^i_{jkl} = E^i_{jkl} - \tfrac{1}{3} S\left(E^i_{jkl} - 2\frac{\delta^i_l E^\alpha_{jk\alpha}}{n-1}\right) + \frac{\delta^i_j E^\alpha_{kl\alpha} + \delta^i_k E^\alpha_{jl\alpha}}{n-1},$$

where

$$E^i_{jkl} = \frac{\partial \Pi^i_{jk}}{\partial x^l} + \Pi^\alpha_{jk}\,\Pi^i_{\alpha l},$$

and S ( ) indicates the sum of the terms obtained by permuting j, k, l cyclically. The Weyl projective curvature tensor[3] is given by

$$W^i_{jkl} = Q^i_{jkl} - Q^i_{jlk}.$$

We leave the question of the other projective invariants given by (3.1) to be treated in a subsequent paper.

* NATIONAL RESEARCH FELLOW IN MATHEMATICS.

[1] Cf. Veblen, these PROCEEDINGS, vol. 8, p. 192.

[2] These quantities were used by T. Y. Thomas in his paper on equi-projective geometry of paths in this volume of these PROCEEDINGS. The parameter which we introduce by means of equations (2.4) is essentially his projective parameter. We had found it before seeing his paper.

[3] Cf. Weyl, *Göttingen Nach.*, 1921, p. 99; also J. M. Thomas, this volume of these PROCEEDINGS.

NOTE ON THE PROJECTIVE GEOMETRY OF PATHS

BY JOSEPH MILLER THOMAS*

PRINCETON UNIVERSITY

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As remarked by T. Y. Thomas in this number of these PROCEEDINGS, the quantities

$$\Pi^i_{jk} = \Gamma^i_{jk} - \frac{\delta^i_j}{n+1}\,\Gamma^\alpha_{\alpha k} - \frac{\delta^i_k}{n+1}\,\Gamma^\alpha_{\alpha j} \qquad (1)$$

have a projective significance in that their value is the same for all affine connections associated with a given system of paths. It is the purpose of this note to show that the projective curvature tensor discovered by Weyl (*Göttingen Nachrichten*, 1921, p. 99) can be expressed in terms of them, and also that they can be used to construct new tensors.

When the coördinates x are subjected to an arbitrary analytic transformation, we have

$$\frac{\partial \bar{x}^i}{\partial x^\alpha}\Pi^\alpha_{jk} = \frac{\partial \bar{x}^\alpha}{\partial x^j}\frac{\partial \bar{x}^\beta}{\partial x^k}\bar{\Pi}^i_{\alpha\beta} + \frac{\partial^2 \bar{x}^i}{\partial x^j \partial x^k} + \frac{1}{n+1}\frac{\partial \bar{x}^i}{\partial x^j}\frac{\partial \log \Delta}{\partial x^k} + \frac{1}{n+1}\frac{\partial \bar{x}^i}{\partial x^k}\frac{\partial \log \Delta}{\partial x^j}, \quad (2)$$

where Δ is the jacobian of the transformation. Differentiation of this relation with respect to x^l followed by an interchange of k and l and a subtraction gives equations which are equivalent to

$$\mathfrak{B}^i_{jkl} = \frac{\partial x^i}{\partial \bar{x}^\alpha}\frac{\partial \bar{x}^\beta}{\partial x^j}\frac{\partial \bar{x}^\gamma}{\partial x^k}\frac{\partial \bar{x}^\delta}{\partial x^l}\bar{\mathfrak{B}}^\alpha_{\beta\gamma\delta} + \delta^i_l\, b_{jk} - \delta^i_k\, b_{jl}, \quad (3)$$

where

$$\mathfrak{B}^i_{jkl} = \frac{\partial \Pi^i_{jk}}{\partial x^l} - \frac{\partial \pi^i_{jl}}{\partial x^k} + \Pi^\alpha_{jk}\,\Pi^i_{\alpha l} - \Pi^\alpha_{jl}\,\Pi^i_{\alpha k}, \quad (4)$$

and

$$b_{jk} = \frac{1}{n+1}\left(\Pi^\alpha_{jk}\frac{\partial \log \Delta}{\partial x^\alpha} - \frac{\partial^2 \log \Delta}{\partial x^j \partial x^k} - \frac{1}{n+1}\frac{\partial \log \Delta}{\partial x^j}\frac{\partial \log \Delta}{\partial x^k}\right).$$

Contracting for i and l in (3) we get

$$b_{jk} = \frac{1}{n-1}\left(\mathfrak{B}^\alpha_{jk\alpha} - \frac{\partial \bar{x}^\beta}{\partial x^j}\frac{\partial \bar{x}^\gamma}{\partial x^k}\bar{\mathfrak{B}}^\alpha_{\beta\gamma\alpha}\right).$$

This result, substituted in (3), gives

$$W^i_{jkl} = \frac{\partial x^i}{\partial \bar{x}^\alpha}\frac{\partial \bar{x}^\beta}{\partial x^j}\frac{\partial \bar{x}^\gamma}{\partial x^k}\frac{\partial \bar{x}^\delta}{\partial x^l}\bar{W}^\alpha_{\beta\gamma\delta}, \quad (5)$$

where

$$W^i_{jkl} = \mathfrak{B}^i_{jkl} + \frac{\delta^i_k}{n-1}\mathfrak{B}^\alpha_{jl\alpha} - \frac{\delta^i_l}{n-1}\mathfrak{B}^\alpha_{jk\alpha}. \quad (6)$$

Equations (5) show that the functions defined by (6) are the components of a tensor which is projective in character since it is defined in terms of the Π's. Substitution from (1) and (4) in (6) gives an expression easily identified with that for the Weyl projective curvature tensor. (Cf. Veblen and Thomas, *Trans. Amer. Math. Soc.*, vol. 25, p. 560.)

Thus the conditions of integrability of the equations (2) of transformation of the Π's give rise to the projective curvature tensor in much the same way that the equations of transformation of the Γ's give rise to the ordinary curvature tensor.

If we differentiate equations (5) with respect to x^ϕ and eliminate the second derivatives of the $\bar{x}$'s by means of (2), we find it is not possible to

eliminate the derivatives of Δ by means of the process of contraction alone. It is readily shown, however, that the following quantities are the components of a projective tensor:

$$W^j_{abc}W^k_{fgh}W^l_{qst}W^p_{uvw}\left(\mathfrak{B}^i_{jklp} - \frac{\delta^i_p}{n-2}\mathfrak{B}^a_{jkla}\right)$$
$$+ \frac{1}{n-2}\,(2W^i_{jkl}W^j_{abc}W^k_{fgh}W^l_{qst}\mathfrak{B}^a_{uvwa} + W^i_{pkl}W^k_{fgh}W^l_{qst}W^p_{uvw}\mathfrak{B}^a_{abca}$$
$$+ W^i_{jpl}W^j_{abc}W^l_{qst}W^p_{uvw}\mathfrak{B}^a_{fgha} + W^i_{jkp}W^k_{abc}W^p_{fgh}W^p_{uvw}\mathfrak{B}^a_{qsta}),$$

where $\mathfrak{B}^i_{jklp}$ is formed from $\mathfrak{B}^i_{jkl}$ in the same way as its covariant derivative but with Π's replacing the Γ's. That the tensor does not vanish identically has been verified by computing one of its components in a special case.

Although this tensor is of a highly complicated form, it is of interest since it indicates the existence of projective tensors other than the Weyl curvature tensor.

* NATIONAL RESEARCH FELLOW IN MATHEMATICS.

DETERMINATION OF THE STRESSES IN A BEAM BY MEANS OF THE PRINCIPLE OF LEAST WORK[1]

BY WILLIAM HOVGAARD

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Introduction.—We owe to Saint-Venant the development of the theory of torsion and bending of beams. In two classic memoirs,[2] equally remarkable for their completeness and lucidity, he has given a rigorous solution of this problem, comprising in particular the determination of displacements, strains and stresses in cylindrical or prismatic beams fixed at one end and loaded at the other.

When the displacements are given, it is an easy matter, by means of the general equations of elastic equilibrium and by a simple differentiation to determine the forces which produce them.

The inverse problem, to determine the displacements when the forces are given, is of far more practical importance, but had not, when Saint-Venant took up the problem, been solved in a general way, on account of the difficulty of integrating the equations in which the displacements enter and of determining the functions and arbitrary constants of integration.

In order to overcome this difficulty, Saint-Venant adopted what he called the mixed or semi-inverse method, intermediate between the two described above. He assumed as given a part of the displacements and a part of the forces and then, by a rigorous analysis he determined what must be the remaining displacements and the remaining forces in order to be compatible with the strain relations as well as with the equilibrium and boundary conditions. In this way he succeeded in obtaining an exact and complete solution and applied it to a great number of particular cases of practical importance.

Saint-Venant's method is most clearly exhibited by stating his assumptions for a specific case, such as that of a cylindrical beam under unequal bending, being fixed at one end and loaded by a vertical force at the other. He assumed as given:

1. A part of the displacements and their relations, in that he supposed the axis to be bent in a plane curve and the elongation (or contraction) of the filaments to be proportional to their distances from a plane through the axis normal to the plane of bending.

2. A part of the forces, in that he supposed that the filaments did not exert on one another any stress normal to their direction, although they could act on each other longitudinally. Further, that no forces acted on the bounding cylindrical surface; and that the resultant force and couple acting on the free terminal section were known, while the mode of application and distribution of these forces were unknown. Finally, that no body forces were acting.

3. The fixation of the beam, in that he supposed the centroid of one of the terminal sections and the central plane element of that section as well as a narrow longitudinal strip in the plane of bending of the axis to be immovable.

Saint-Venant now showed that these assumptions were compatible between themselves, and next determined the still unknown displacements and stresses as well as the distribution of the external forces which acted on the free terminal section.

In the solution here offered, the inverse method, referred to above, is followed. All the external forces as well as their distribution over the end section are assumed to be known, while none of the displacements are given. By means of the Principle of Least Work or Minimum Energy the stresses are determined and from these the displacements can be found. By the use of this Principle and the Calculus of Variation it is possible to embody all the conditions together with the expression for the elastic work of deformation in one integral, by the variation of which the unknown stresses can be determined directly. The solution comprises all possible conditions of loading of the beam at the free end and being based on the fundamental principle of Least Work, gives assurance that the state of stresses to which it leads, is one to which the beam must tend, even although it may not in practice conform to it near the points of application of the external forces. In other words, it gives the ideal or natural stress distribution.

The general solution for the stresses contains unknown arbitrary functions, which are determined by integration of two partial differential equations of the second order and the solution must at the same time fulfil certain boundary conditions.

Statement of the Problem.—Consider the state of stress in a cylindrical or prismatic beam of any form of section and of isotropic material, fixed at one end, while at the terminal section of the free end and a system of forces is applied. No external forces act on the lateral bounding surfaces and the action of gravity is neglected.

The axis of the beam is supposed to be horizontal and a rectangular system of coördinates is placed so that the origin, O_0, is at the center of gravity of the fixed section; $O_0 Z$ coincides with the axis, while $O_0 X$ and $O_0 Y$ coincide with the principal axes of the section. To fix ideas we take $O_0 X$ to be vertical, positive downwards and $O_0 Y$ horizontal, positive to the left when looking from the outer end A towards O_0. The directions

of rotation are positive from O_0X to O_0Y, O_0Y to O_0Z, and O_0Z to O_0X. The length of the beam is $l = O_0A$.

When dealing with any section between O_0 and A we use a system of coördinates with axes in the same directions as at O_0 but with origin at O, the centroid of the section.

The system of forces acting on the free end represents the most general case and may be resolved in the following resultant forces and couples:

An axial force P, a vertical force Q, and a horizontal force S all acting at the center of gravity of the terminal section at A. A torsional couple T with axis parallel to O_0A, a bending couple M_{VA} in the vertical plane and a bending couple M_{HA} in the horizontal plane. The couples produce uniform twisting or bending moments throughout the length of the beam, but the forces Q and S produce bending moments which increase from zero at A to Ql and Sl, respectively, at O_0. Thus at any point distant z from O_0 we have the total bending moments:

$$M_V = M_{VA} + Q\,(l - z), \quad M_H = M_{HA} - S\,(l - z) \tag{1}$$

It is assumed that the distribution of the external forces over the terminal section at A is such as to conform to the yet unknown stress distribution required by the Principle of Least Work. The same assumption is made for the reactions over the section at the fixed end. Thus all the forces are known or determinate and the problem is to find the stresses, which are all unknown.

It is assumed that the fixation of the beam is established in the same way as defined by Saint-Venant, and, as assumed by him, there are no normal transverse stresses, that is, the longitudinal filaments, of which we may imagine the body to be made up, do not exert on each other any pressures or tensions normal to their direction. Also transverse tangential tractions in planes parallel with the axis are neglected. On the other hand, when the fibers move lengthwise relative to one another shear stresses are created.

There remain to be considered only three stresses: a longitudinal normal stress p and two shear stresses, q and s, which act, respectively, vertically and horizontally in planes normal to the axis. The shear stresses comprise correlated tangential tractions acting longitudinally.

It follows that the strain in direction of OZ is: $e_{zz} = p/E$, where E is Young's modulus of elasticity, and the strain components due to shearing are:

$$e_{zx} = q/G,\ e_{zy} = s/G, \qquad e_{xx} = e_{yy} = -\sigma e_{zz} = -\sigma p/E \tag{2}$$

where σ is Poisson's ratio and G is the coefficient of rigidity. It is assumed that E and G are related by the equation:

$$G = \tfrac{1}{2}\,E/(1 + \sigma)$$

The Elastic Work of Deformation and the Equations of Condition.—The elastic work of deformation, expressed in terms of the stresses, takes the simple form:

$$W = \int_{x_2}^{x_1}\int_{y_2}^{y_1}\int_0^l \left\{\frac{p^2}{2E} + \frac{q^2}{2G} + \frac{s^2}{2G}\right\} dxdydz \tag{3}$$

The stresses p, q, and s are unknown functions of x, y and z, but must be such as to make the elastic work a minimum while at the same time satis-

fying the conditions of equilibrium, the boundary conditions, and certain equations of compatibility of the strains.

The equations of condition are the following:

1. For equilibrium of an elemental prism we have:

$$\partial q/\partial z = 0 \text{ and } \partial s/\partial z = 0 \quad (4), \qquad \partial q/\partial x + \partial s/\partial y + \partial p/\partial z = 0 \quad (5)$$

It follows from (4) that q and s are independent of z, whence the shear stresses are the same at any set of values (x, y) throughout the beam, i.e., the tangential tractions are identically alike on every transverse section.

2. The strain components must comply with certain equations of compatibility, which, expressed in terms of the stresses according to (2), furnish the relations:[3]

$$\frac{1}{G}\frac{\partial}{\partial y}\left[\frac{\partial s}{\partial x} - \frac{\partial q}{\partial y}\right] + 2\frac{\sigma}{E}\frac{\partial^2 p}{\partial z \partial x} = 0 \qquad (6)$$

$$\frac{1}{G}\frac{\partial}{\partial x}\left[\frac{\partial s}{\partial x} - \frac{\partial q}{\partial y}\right] - 2\frac{\sigma}{E}\frac{\partial^2 p}{\partial z \partial y} = 0 \qquad (7)$$

3. At any transverse section we must have:

$$P = \int\int p\,dxdy \quad (8), \qquad Q = \int\int q\,dxdy \quad (9), \qquad S = \int\int s\,dxdy \quad (10)$$

$$T = \int\int (sx - qy)\,dxdy \qquad (11)$$

$$M_V = M_{VA} + Q\,(l - z) = -\int\int px\,dxdy \qquad (12)$$

$$M_H = M_{HA} - S(l - z) = \int\int py\,dxdy \qquad (13)$$

The integration in all these integrals to extend over the entire surface of the cross section.

4. At the lateral bounding surface the sum of the stress components normal to the surface must be zero since no external forces act on that surface. Let the equation to the bounding curve of a transverse section be:

$$y = \phi\,(x) \quad \therefore dy/dx = d\phi/dx \qquad (14a)$$

Then:

$$s/q = dy/dx = d\phi/dx \qquad (14b)$$

at all points of the boundary.

The Variation.—In forming the variational integral U we follow the method of Lagrange. The expressions on the left side of the differential equations (5), (6) and (7) are multiplied by coefficients which are functions of the independent variables and are entered under the integral sign of (4), but since there are only three indeterminate quantities we can have only two independent conditions, and hence, shall need only two

arbitrary coefficients. We therefore introduce the functional coefficients λ_1 for equation (5) and λ_2 for the sum of (6) and (7).

Each of the expressions under the integral sign in (8) to (13) is now multiplied by a constant, a, b, c, e, f, g, respectively, and added under the integral sign of (3), and we get:

$$U = \int_{x_2}^{x_1}\int_{y_2}^{y_1}\int_0^l \left\{ \frac{p^2}{2E} + \frac{q^2}{2G} + \frac{s^2}{2G} + ap + bq + cs + e(sx - qy) + fpx + gpy + \lambda_1\left(\frac{\partial q}{\partial x} + \frac{\partial s}{\partial y} + \frac{\partial p}{\partial z}\right) + \lambda_2\left(\frac{1}{G}\frac{\partial^2 s}{\partial y \partial x} - \frac{1}{G}\frac{\partial^2 q}{\partial y^2} + 2\frac{\sigma}{E}\frac{\partial^2 p}{\partial z \partial x} + \frac{1}{G}\frac{\partial^2 s}{\partial x^2} - \frac{1}{G}\frac{\partial^2 q}{\partial x \partial y} - 2\frac{\sigma}{E}\frac{\partial^2 p}{\partial z \partial y}\right)\right\} dxdydz \qquad (15)$$

In order to make U a minimum it is necessary that the variation of U shall be zero when p, q and s are made to vary independently and arbitrarily by an infinitesimal amount. The variation consists of two parts, first the terms at the limits, three groups of double integrals depending on the variations of p, q and s and of their derivatives for such values of the independent variables as satisfy the boundary equations; second, of one triple integral depending on entirely arbitrary variations of p, q and s. The terms at the limits all vanish, and we have:

$$\delta U = \int_{x_2}^{x_1}\int_{y_2}^{y_1}\int_0^l \left\{ \left[\frac{p}{E} + a + fx + gy - \frac{\partial \lambda_1}{\partial z} + \frac{2\sigma}{E}\frac{\partial^2 \lambda_2}{\partial z \partial x} - \frac{2\sigma}{E}\frac{\partial^2 \lambda_2}{\partial z \partial y}\right]\delta p + \left[\frac{q}{G} + b - ey - \frac{\partial \lambda_1}{\partial x} - \frac{1}{G}\frac{\partial^2 \lambda_2}{\partial y^2} - \frac{1}{G}\frac{\partial^2 \lambda_2}{\partial x \partial y}\right]\delta q + \left[\frac{s}{G} + c + ex - \frac{\partial \lambda_1}{\partial y} + \frac{1}{G}\frac{\partial^2 \lambda_2}{\partial y \partial x} + \frac{1}{G}\frac{\partial^2 \lambda_2}{\partial x^2}\right]\delta s \right\} dxdydz \qquad (16)$$

Solution for the Longitudinal Stress.—We assign to λ_1 and λ_2 such values as shall make the factors of δq and δs vanish and it follows that also the factor of δp must then be made equal to zero in order to make the triple integral vanish.

Equating the factors of δq and δs to zero, we obtain expressions for q and s in terms of x, y, λ_1 and λ_2, but since q and s are independent of z according to (4), the coefficients λ_1 and λ_2 can be functions of x, y only. Hence the three differentials with respect to z of these coefficients, which occur in the factor of δp must vanish and by equating the remaining terms to zero we obtain the equation:

$$p = -E(fx + gy + a) \qquad (17)$$

Substituting in (8), we get:

$$P = -E \int\int (fx + gy + a)\, dxdy = -E\,(fm_y + gm_x + aA)$$

where m_y and m_x are the area moments of the section about the X-axis and Y-axis respectively, through the centroid and A is the area of the section. Since OX and OY are by supposition the principal axes, m_y and m_x vanish and we get:

$$a = -P/AE = -p_0/E \tag{18}$$

where p_0 is the mean longitudinal stress in the beam due to the longitudinal force P.

Substituting the value of p from (17) in (12) and (13) we get:

$$M_{VA} + Q(l - z) = E \int\int (fx^2 + gxy + ax)\, dxdy = EfI_y$$
$$M_{HA} - S(l - z) = -E \int\int (fxy + gy^2 + ay)dxdy = -EgI_x$$

where I_y and I_x are the moments of inertia of the section about the axes OX and OY, respectively, while all integrals containing odd powers of x and y vanish. Hence

$$f = \frac{M_{VA} + Q(l - z)}{EI_y} \text{ and } g = -\frac{M_{HA} - S(l - z)}{EI_x} \tag{19}$$

Substituting these values of the constants in (17), we find:

$$p = -\frac{M_{VA} + Q(l - z)}{I_y}\, x + \frac{M_{HA} - S(l - z)}{I_x}\, y + p_0 \tag{20}$$

The first term in this expression taken by itself gives the usual formula for bending in the vertical plane. It consists of one part corresponding to a uniform bending moment due to the couple M_{VA} and another part due to the vertical end load Q. The second term gives the corresponding formula for bending in the horizontal plane, both being of the general form:

$$p = Mx/I \tag{21}$$

This is the ordinary formula for bending stresses, which is thus seen to be in accordance with the Principle of Least Work not only in case of uniform bending in a circle but also for unequal bending.

The third term in (20) represents a longitudinal stress due to the axial force P. Since neither x nor y enter into this term, we may infer that for Least Work this stress must be uniformly distributed.

It is now possible to simplify the factor of λ_2 in (15). From (20) we find:

$$\frac{\partial^2 p}{\partial z \partial x} = \frac{Q}{I_y} \text{ and } \frac{\partial^2 p}{\partial z \partial y} = \frac{S}{I_x} \tag{22}$$

whence by substitution in (6) and (7) and integration we obtain:

$$\frac{\partial s}{\partial x} - \frac{\partial q}{\partial y} = 2\tau g + \frac{2\sigma G}{E}\left[\frac{Sx}{I_x} - \frac{Qy}{I_y}\right] \tag{23}$$

where τ is a constant of integration. The expression on the left side of (23) takes the place of (6) and (7) in the factor of λ_2 in equation (15), and thus the triple integral in δU becomes:

$$\int_{x_2}^{x_1}\int_{y_2}^{y_1}\int_0^l \left\{\left[\frac{p}{E} + a + fx + gy\right]\delta p + \left[\frac{q}{G} + b - ey - \frac{\partial\lambda_1}{\partial x} + \frac{\partial\lambda_2}{\partial y}\right]\delta q + \left[\frac{s}{G} + c + ex - \frac{\partial\lambda_1}{\partial y} - \frac{\partial\lambda_2}{\partial x}\right]\delta s\right\} dxdydz = 0 \qquad (24)$$

We have already disposed of the factor of δp and equating now the factors of δp and δs to zero we find:

$$q = G\left[\frac{\partial\lambda_1}{\partial x} - \frac{\partial\lambda_2}{\partial y} + ey - b\right], \qquad s = G\left[\frac{\partial\lambda_1}{\partial y} + \frac{\partial\lambda_2}{\partial x} - ex - c\right] \qquad (25)$$

from which by differentiation and substitution in (5) and (23):

$$\frac{\partial^2\lambda_1}{\partial x^2} + \frac{\partial^2\lambda_1}{\partial y^2} = -\frac{1}{G}\left[\frac{Qx}{I_y} + \frac{Sy}{I_x}\right] \qquad (26)$$

$$\frac{\partial^2\lambda_2}{\partial x^2} + \frac{\partial^2\lambda_2}{\partial y^2} = 2(\tau + e) + \frac{2\sigma}{E}\left[\frac{Sx}{I_x} - \frac{Qy}{I_y}\right] \qquad (27)$$

We have now arrived at the general solution of the problem, comprising two partial linear differential equations of the second order, but the integration of these in any given case depends upon the possibility of finding such expressions for λ_1 and λ_2 as will satisfy the boundary conditions. This part of the problem depends upon the form of the contour of the transverse sections and can be completely and accurately solved for a number of sections of simple form.

The following solution, comprising only rational integral algebraical functions of x and y, satisfies the boundary conditions for various simple sections with one or two axes of symmetry.

$$\lambda_1 = B(y^3 - 3yx^2) + C(x^3 - 3xy^2) - \left[\frac{Sx}{I_x} + \frac{Qy}{I_y}\right]\frac{xy}{2G}$$
$$\lambda_2 = (\tau + e)x^2 + \frac{\sigma}{3E}\left[\frac{Sx^3}{I_x} - \frac{Qy^3}{I_y}\right] \qquad (28)$$

Differentiate λ_1 and λ_2 and substitute in (25):

$$q = G\left[3C(x^2 - y^2) - \left(6B + \frac{S}{GI_x}\right)xy - \frac{Qy^2}{EI_y} + ey - b\right] \qquad (29)$$

$$s = -G\left[3B(x^2 - y^2) + \left(6C + \frac{Q}{GI_y}\right)xy + \frac{Sx^2}{EI} - (2\tau + e)x + c\right] \qquad (30)$$

The three constants b, c and e can be determined from (9), (10) and (11), respectively, and the three constants of integration τ, B and C from the boundary conditions.

In case of simple bending in a plane of symmetry without any other action, the stresses must be the same at corresponding points with reference to the axis of symmetry. For instance, in case of a vertical end load acting alone, q must be the same for $+y$ and $-y$ for a given value of x. Hence we cannot have y to the first power in the expression for q, and it follows that $B = 0$ and $e = 0$. Moreover $S = 0$. For a horizontal end load acting alone in a plane of symmetry we must have $Q = 0, C = 0$, $\tau = 0$, $e = 0$.

For a beam with two axes of symmetry under a pure torsional couple and in the absence of bending there can be no terms of even power in x or y in the expressions for the stresses, whence B and C must vanish. In that case also terms containing Q and S vanish and $b = c = 0$. Substituting the resulting values of q and s in (11) we have the torsional couple

$$T = G \int\int [(2\tau + e)x^2 - ey^2]\, dxdy = 2\tau G + e(I_y - I_x) \quad (31)$$

where the integration is to extend over the entire area of the section. When $T = 0$ we have $e = 0$ and it follows also that $\tau = 0$ in the cases to which (29) and (30) apply.

For sections of rectangular form it is necessary to introduce transcendental series in the solution of (26) and (27).

Thus it is shown that by means of the Principle of Least Work it is possible to determine the stresses, when the external forces acting on the beam are known without making any a priori assumptions regarding the displacements as by Saint-Venant's method.

We have assumed that the forces at the free end and the reactions at the fixed end are distributed over the terminal sections in accordance with the stress distribution prescribed and subsequently determined by the Principle of Least Work. In practice these conditions are never fulfilled, but as there is an inherent tendency of the stresses to conform to that principle, we are justified in asserting that at a certain distance from the terminals the stresses will adjust themselves in accordance therewith. This confirms Saint-Venant's principle of the elastic equivalence of statically equipollent systems of load.

[1] A more detailed account will appear in *J. Math. Physic.*, Mass. Inst. Tech., Vol. 4, 162 (1925).

[2] B. de Saint-Venant: "La Torsion des Prismes," *L'Académie des Sciences*, **14** (1856); "La Flexion des Prismes," Liouville's *J. Math.*, 2 ser., **1** (1856).

[3] A. E. H. Love, "Theory of Elasticity," 1920, p. 50.

RESEARCHES ON SELENIUM ORGANIC COMPOUNDS. V. A SIMPLE METHOD FOR THE SYNTHESIS OF 2-SUBSTITUTED BENZOSELENAZOLES[1]

BY MARSTON TAYLOR BOGERT AND CARL NORMAN ANDERSEN

ORGANIC LABORATORIES, COLUMBIA UNIVERSITY

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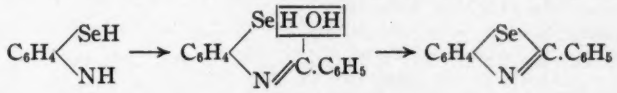
Introductory.—One of the simplest and most satisfactory methods for the preparation of benzothiazoles is that discovered by Hofmann[2] in 1879, which consists in the condensation of acyl halides or anhydrides with *o*-aminoaryl mercaptans. Recent improvements in details[3,4,5] have added considerably to its convenience and efficiency.

In the continuation of our study of the benzoselenazoles[6,7] it seemed desirable to attempt the synthesis of such compounds from the *o*-aminoaryl selenophenols by this method, and its availability has been proven by the preparation of 2-phenylbenzoselenazole by the following steps:



The method will be utilized for the production of other benzoselenazoles and related compounds as opportunity offers.

Experimental Part.—(1) *o-Nitrophenyl Diselenide,* $(O_2NC_6H_4)_2Se_2$.—To a solution of 50 g. of sodium selenide in 150 cc. of warm alcohol, 12 g. of finely powdered selenium was added and the mixture refluxed on the steam bath. The selenium soon dissolved with formation of a reddish brown liquid. This hot alcoholic solution of sodium diselenide was poured into a hot solution of 32 g. of *o*-nitrochlorobenzene in 50 cc. of alcohol. Sodium chloride separated immediately. The mixture was refluxed for two hours and then allowed to cool. The crude product appeared as a brownish mass; yield, 80%. By repeated solution in hot glacial acetic acid, followed by careful dilution, a yellowish brown amorphous solid was obtained, which was washed with boiling alcohol and then melted at 206.2–206.5° (corr.). The yield of this purified product was low. For analysis, it was dried two hours at 120°.

Anal. Calc. for $C_{12}H_8N_2O_4Se_2$: C, 35.82; H, 1.99. Found: C, 35.95; H, 2.11.

(2) *o-Aminoselenophenol.*—Zinc dust was added gradually to a gently boiling solution of 4 g. of the crude nitrophenyl diselenide in 500 cc. of glacial acetic acid, until the color of the solution was discharged, which occurred usually in about five minutes. Longer heating (30–60 minutes) with excess of zinc dust, appeared to destroy much of the product.

The boiling solution was filtered rapidly, by means of a Buchner funnel, into a large volume of water, and the zinc salt then precipitated in crystalline form. It was washed first with water, then with boiling alcohol and dried; yield, 0.7 g.

Anal. Calc. for $C_{12}H_{12}N_2Se_2Zn$: Zn, 15.96. Found Zn, 15.61.

(3) *2-Phenylbenzoselenazole.*—A mixture of 0.89 g. of zinc *o*-aminoselenophenolate with 1 g. of benzoylchloride was heated for 30 minutes at 100°. The crude product (0.5 g.) was boiled for 30 minutes with 100 cc. of N NaOH, decolorized, and crystallized from alcohol. Straw-colored crystals were obtained, m. p. 117° (corr.). This product was identical in chemical and other physical properties with 2-phenyl-benzoselenazole prepared by a different method, and an intimate mixture of the two melted sharply at the same point.

Summary.—*2-Phenylbenzoselenazole* can be prepared from *o*-aminoselenophenol and benzoyl chloride by a procedure similar to that used for the synthesis of benzothiazoles from *o*-aminothiophenols and acyl halides.

[1] Contribution from the chemical laboratories of Columbia University No. 467.
[2] Hofmann, *Ber.*, **12**, 2362, 2365 (1879).
[3] Blanksma, *Rec. trav. chim.*, **20**, 121 (1901).
[4] Wohlfahrt, *J. prakt. Chem.* [2], **66**, 553 (1902).
[5] Bogert and Snell, *J. Am. Chem. Soc.*, **46**, 1308 (1924).
[6] Bogert and Chen, *Ibid.*, **44**, 2352 (1922).
[7] Bogert and Hopkins, *Ibid.*, **46**, 1700, 1912 (1924).

THE REFLECTION OF X-RAYS BY ALKALI HALIDE CRYSTALS

BY ALICE H. ARMSTRONG, WILLIAM DUANE, R. J. HAVIGHURST[1]

CRUFT LABORATORY, HARVARD UNIVERSITY

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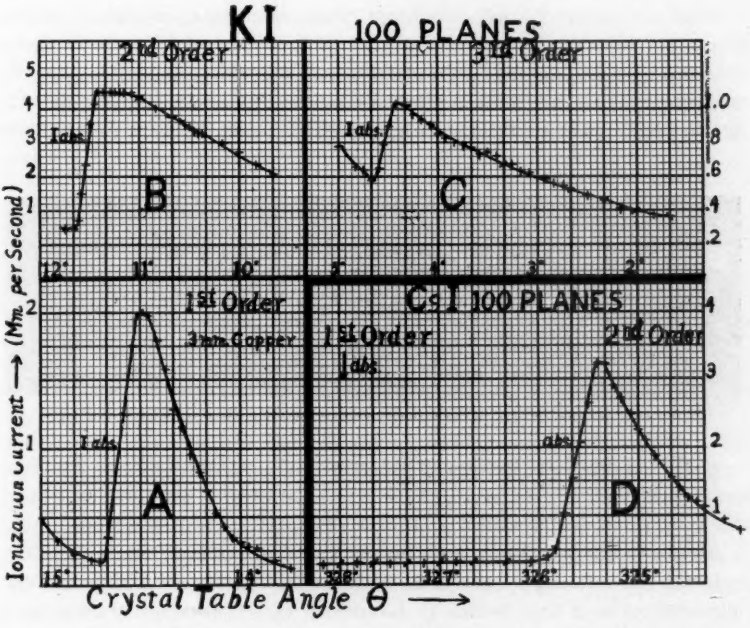
On examining the reflection of X-rays by certain potassium iodide crystals, we observed marks on the photographic films indicating peculiar ways in which the crystals grew together. For instance, when one of the potassium iodide crystals was so placed as to reflect X-rays from the 100 planes, a double image appeared. In addition to this double image, however, with long exposures, a series of very fine lines could be seen indicating the presence of very small crystals displaced from their normal positions. They did not occur in random positions, but in positions such that their axes were parallel to that of the main crystal. This peculiar method of formation together with the fact that the wave-lengths near the *K* series lines of iodine are transmitted through the crystals with very much greater intensity than other wave-lengths explains a great

many of the peculiar abnormal reflections previously observed with alkali halide crystals. Dickinson has suggested that certain diffuse spots on Laue photographs may be due to reflections by minute crystals making small angles with the main crystals.

Photograph 1 represents the impression produced by the continuous spectrum of X-rays from a tungsten target reflected from a potassium iodide crystal. The angle of incidence is about that required to reflect the α line in the K series of iodine from the 100 planes. The two images appear and also the fine lines representing small, displaced crystals. These lines extend toward the right but stop abruptly at a point corresponding



to the critical absorption wave-length of iodine, the wave-length at which the iodine begins to absorb the X-rays very strongly.

Photograph 2 represents the effect produced by rays reflected by the same crystal but at a glancing angle of incidence corresponding to the β line in the K series of iodine. The double image appears and also a series of fine lines, but now, on the left of the main image. It may be that the fine lines are too weak in this case to be seen on the *reproduction* of the photograph.

The main impressions on films 3 and 4 are due to X-rays reflected by

the same crystal at angles corresponding to wave-lengths shorter than the K series of iodine (about 0.3 or 0.33). These wave-lengths are very heavily adsorbed by the crystal and long times of exposure are required to produce the impressions. A second impression appears on each film, which looks like an abnormal reflection from the crystal. This may be explained, however, by supposing that it is due to wave-lengths between the α and β lines in the K series of iodine (for which the crystal is very transparent) reflected by some of the very small, displaced crystals. If these crystals had been oriented at random, we would expect more or less of a complete circle to appear in the photograph. The orientation with axes parallel to the main axis, however, confines the reflection to certain directions only.

After a number of trials, we found some crystals of potassium iodide which did not show this phenomenon to a very marked degree. We have used one of these crystals to obtain spectrum curves by the ionization spectrometer. They appear at A, B and C in the figure. A 50,000 volt storage battery furnished the current through the tube in these experiments

and kept the voltage extremely constant. Curve A represents the first order reflection of the continuous X-ray spectrum, after the rays had passed through a filter of 0.3 millimeter of copper. The marked rise in the ionization curve corresponds to the critical absorption of iodine. On the long wave-length side of the peak the curve shows a very sharp decline. The sharpness of this decline is due partly to the filtration of the copper and partly to the filtration of the crystal itself. Curves B and C represent second and third order reflections of the continuous X-ray spectrum by the same crystal. In each case, the critical absorption of the K series of iodine is sharply marked by the rapid rise in the curve. None of these curves indicate strong reflection of the $K\alpha$ line of iodine. There are no well-marked humps or peaks on the long wave-length sides of the critical absorptions, as observed in many previous experiments.

Curve D represents the reflection of the continuous X-ray spectrum by the 100 planes of cesium iodide. Here the critical absorption of cesium and iodine is sharply marked in what we may call the second order spec-

trum. There is no evidence for the reflection of the $K\alpha$ and $K\beta$ lines in the second order spectrum. The first order spectrum could not be detected at all. The position where the critical absorption should come in the first order is marked in the diagram. The height of the curve in the neighborhood of this point above the base line represents the ionization current due to stray radiation, etc., and we were not able to detect any true reflection of X-rays in this first order. Owing to the fact that in cesium iodide, which has a body-centered structure, the 100 planes alternate between cesium and iodine, such a first order reflection would be expected, if there were an appreciable difference between the radiation reflected by the iodine planes and that reflected by the cesium planes.

On using very tall slits on an ionization spectrometer, it sometimes happens that X-rays reflected by tilted planes such as the 131 planes enter the ionization chamber. If it happens that these tilted planes reflect X-rays whose wave-lengths lie near the K series lines of a chemical element in the crystal, these reflections become very strong. We have examined a number of such reflections and find that the critical voltages at which they appear indicate wave-lengths lying usually between the $K\alpha$ and $K\beta$ lines.

It appears from these experiments that when reasonably good crystals are employed which do not have a marked structure of the kind above described, the spectrometer curves show no abnormal peaks corresponding to reflection of the characteristic iodine, etc., radiation. The spectrum curves are normal and precisely what one would expect, taking into account the fact that the X-rays are characteristically absorbed by the iodine, etc., in passing through the crystals. It seems probable that many of the reflections of characteristic lines previously observed may have been due to this peculiar way that the crystals have of growing together. The fact that the observed critical voltages at which these reflections appeared corresponded with wave-lengths equal to or near to those of the K series lines of iodine favors this view; for the crystal has a very great transparency for X-rays of just those wave-lengths.

[1] NATIONAL RESEARCH FELLOW.

NOTE ON THE DIFFRACTION OF X-RAYS BY A WEDGE-SHAPED SLIT

By Irwin Isaac Rabinov

Ryerson Physical Laboratory, University of Chicago

Communicated October 22, 1924

The works of the previous investigators[1] disagree fundamentally as to the presence of diffraction fringes—of the same nature as those obtained from ordinary light—when X-rays pass through a wedge-shaped slit.

The author[2] using a slit which was similar to those of the other workers but which did not have parallel faces (the faces made a dihedral angle of 25° with each other) obtained results which were very much the same as

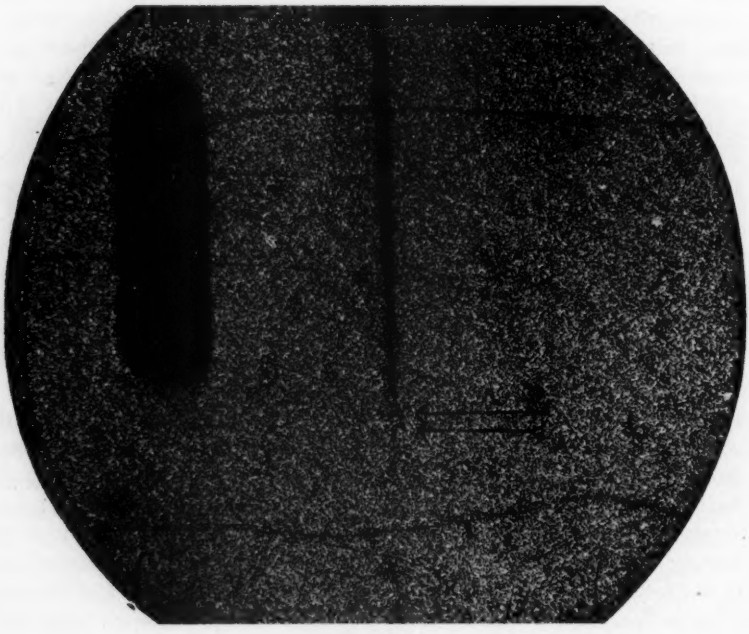


FIGURE 1

those of Haga and Wind, indicating a widening but no separation. The wave-lengths calculated from the simple theory of diffraction gave an average wave-length for the general radiation from tungsten of 0.46Å. No individual wave-length could be determined since continuous radiation was used (K.V. = 46).

The work was repeated still more carefully using a V-shaped slit with faces parallel to the X-ray beam, and was very successful. This time a fine fringe was obtained at the lower end (fig. 1) for the K-alpha line of molybdenum alone. This was accomplished by placing a crystal of calcite before the first slit in such a manner as to send through that slit the K alpha$_1$ and K alpha$_2$ lines. When the V-shaped slit was correctly placed—and only then—the K alpha$_1$ line passed through.

The rays from a molybdenum target Coolidge X-ray tube operated at 46 K.V. struck the crystal. The characteristic K rays were reflected through S_1 a parallel adjustable platinum-iridium slit of 0.1 mm. width and were then diffracted by the V-slit S_2 at a distance of 186.5 cms. from S_1. The slit S_2 was also of platinum-iridium. The diffracting wedge was 2 cms. long, 0.03 mm. wide at the top, and tapered to zero at the bottom. The plate holder was placed at 186.5 cms. from S_2.

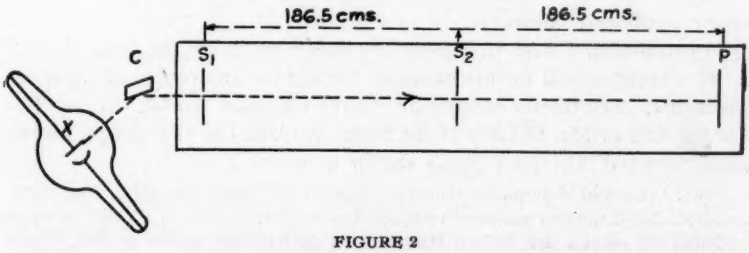


FIGURE 2

The K alpha line from the molybdenum target x, was reflected from the crystal C through the slit S_1, and the diffraction pattern due to S_2 appeared at P. The target was placed so that a very narrow bundle of rays left the tube and was reflected from the crystal.

The platinum slits were both mounted on brass plates in which narrow slits were cut along their entire length. The parallel slit had a screw adjustment to vary its width; the wedge slit was changed by loosening the screws in the brass, pressing the platinum wedge together while again tightening the screws.

Rotations about every axis were possible for both slits and the plate holder, and it was thus only a question of time before accurate adjustments could be attained. Figure 2 is a diagram of the diffracting apparatus. Vibrations of every sort made the work of adjustment very difficult even when the whole apparatus rested on a long I-beam but even these were finally eliminated.

Continuous exposures of from a few minutes up to 12 days and 12 nights were taken, figure 1 being for 12 days and 12 nights with a 25-fold magnification. It shows quite clearly the single fringe gradually widening and separating from the main band until visible to the naked eye. The curva-

ture of the band is quite appreciable and is to be expected from such a slit.

Using the simple theory of diffraction for a single slit we find, that if the wave length for the molybdenum rays is 0.7Å and the total width of the fringe is (at the position of the upper arrow in figure 1) 0.55 cm., then the slit width must be 0.0018 mm. If the width corresponding to the position of the lower arrow is taken where the width is 0.74 cm. then the slit width comes out 0.0013 mm. At the position where diffraction first definitely begins, the slit width to have produced that widening is 0.004 mm. This is in agreement with the work of Haga and Wind. As is now quite apparent, the great difficulty, once the fringe is obtained is to measure correctly the slit width corresponding to the point of measurement of the fringe width.

Even with the present decisive photograph it does not seem possible to obtain the wave-length of the X-rays with accuracy because of the above-mentioned difficulty.

In conclusion, I wish to express my appreciation for the help of Prof. A. H. Compton and for his kindness throughout the course of these experiments. My thanks are also due to the Eastman Kodak Co., of Rochester and to Mr. M'Ghee of the Sweet Wallack Co. of Chicago, for the enlargement of the photograph shown in figure 1.

NOTE: At the time of the publication of this paper Herr Walter (*Ann. Phys.*, Aug., 1924, and Sept., 1924) had just published two papers on the "Diffraction by a V-Slit" in which he found the effect which, before, Walter and Pohl had been unable to find. Their new measurements are with the long rays from copper (1.54Å). It is interesting to note that in figure 1 the separation is complete and the fringe diverges in a fan-shape while in the photograph of Walter the first order bands do not diverge very much from the main band.

[1] Haga and Wind, *Ann. Physik.*, **68**, 884, 1903; Walter and Pohl, *Ibid.*, **29**, 331, 1909; Sommerfeld, "Atombau u. Spectral," pp. 118–120, 1919 ed.

[2] Irwin Isaac Rabinov, M.S., *Thesis*, University of Chicago, Nov., 1923.

THE COMPTON EFFECT WITH HARD X-RAYS

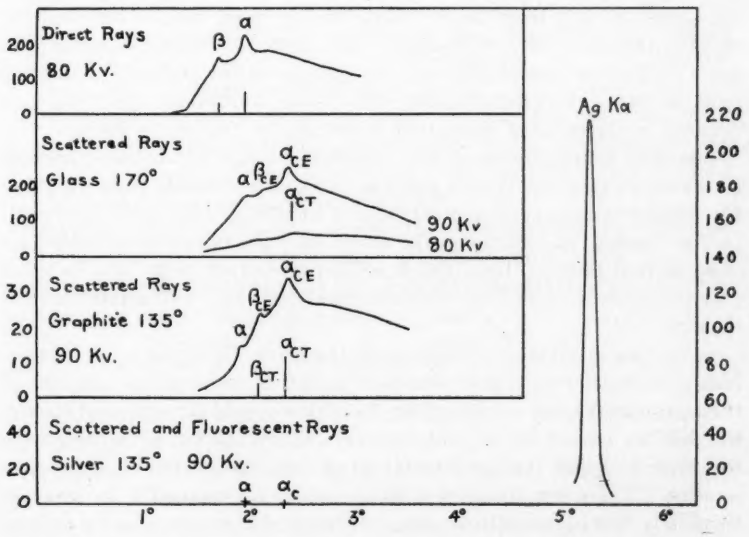
BY D. L. WEBSTER AND P. A. ROSS

STANFORD UNIVERSITY, CALIFORNIA

In the researches on the Compton effect published to date, the region least known is that of hard X-rays, where recent statements as to its existence are quite conflicting. At the December meeting of the American Physical Society, we reported finding the Compton effect in hard rays, but the data covered so few cases, and those with such an unsatisfactory degree of accuracy, that we hoped to improve them before more detailed

publication. Unfortunately, however, the work was then unavoidably interrupted, so it seems advisable now to support our assertion for the existence of this effect by publishing what evidence we have, in spite of its incompleteness.

The spectrometer used in this work was an ionization instrument with a Dolezalek electrometer and a slit system in which the angular width of the beam was limited by two slits, one an ordinary lead slit, very near the scattering block, and the other a Seemann slit with a gold edge. In addition to these, there were five wider slits, or diaphragms, for stopping stray rays. This two-slit combination avoids any of the irregularities of intensity to which Soller slits would be liable if used at these very small glancing angles.



The tube was a special water-cooled tungsten-target tube with no bulb, the glass being a single cylindrical tube of 3.6 cm. diameter, enabling us to place the scattering block very close to the focus. In spite of its small diameter, however, this tube would stand potentials up to 90,000 volts. For the privilege of using this remarkable tube, we are indebted to the General Electric Co., and especially to Drs. Coolidge and Davey, who designed it and had it built for us.

The results of this preliminary survey are shown in figure 1. In this figure the upper graph is a direct-ray spectrum, obtained at 80 kv. during the process of seasoning the tube, and showing the tungsten *K*-series lines,

which were used as wave-length standards for locating the zero of the spectrometer scale.

The pair of graphs below this one were obtained with the rays scattered from glass, primarily the glass of the X-ray tube on the side farthest from the slits, but supplemented by a plate of glass beyond the tube. This scatterer has the disadvantage of heterogeneity of composition, especially as the plate unfortunately turned out to be lead glass; and it is also impossible to be sure that the glass in the nearer side of the tube in line with the slits was all in the shadow of the target. But it had the advantage of giving the strongest scattered rays obtainable, and this proving most conclusively the existence of the Compton peaks. In these curves, the experimental points are crowded together too closely to show on this scale, there being 45 of them in all. Their departures from the curve are almost all less than the width of the line used here to represent it, and the position of the shifted peak, α_{CE}, agrees to within two minutes of arc with the theoretical position, α_{CT}, an agreement probably within the limit of error. Incidentally, the shift of the continuous spectrum as a whole is of the order of magnitude predicted by Compton's theory.

The next graph, obtained with graphite, is not so accurate, because the available intensity is only about a fifth that obtainable from the glass. But still its 42 experimental points depart from it by only about 2 per cent, on the average, and all the peaks shown here are distinctly indicated by experimental points. Here the experimental shifted peak, α_{CE}, is again only two minutes of arc from the theoretical peak, α_{CT}, well within the limit of error.

In the case of silver, at the bottom of the figure, the α line of the fluorescent rays was the strongest secondary radiation we obtained from any of these substances, and presumably the β line would have proved strong, too, had we looked for it; but elsewhere in the spectrum the rays were too weak to detect, except possibly at or near the unshifted tungsten α position. There we obtained a faint radiation, impossible to measure accurately, but apparently about a two-hundredth as strong as the fluorescent rays. This is in very sharp contrast to the results of Clark and Duane,[1] but in complete agreement with results obtained photographically in 1914 by de Broglie,[2] who states that fluorescent spectra are almost free from "white" radiation, and it is likewise to be expected from the figures found in the classical researches by which Barkla[3] discovered X-ray fluorescence.

In conclusion we must emphasize again the purely preliminary character of these results, and the fact that they are not accurate enough to warrant quantitative conclusions on the relative intensities of the peaks, although for glass and graphite they do demonstrate that the Compton effect exists and that the line showing the Compton shift is strong.

[1] G. L. Clark and W. Duane, these PROCEEDINGS, **10**, 92, March, 1924.
[2] M. de Broglie, *Comptes Rendues Paris Acad. Sci.*, **158**, 1493 (1914); *Journal de Physique* (July, 1916).
[3] See especially *London Phil. Mag.*, **16**, 550 (1908).

THE HEAT CAPACITY OF SOLID ALIPHATIC CRYSTALS

BY E. O. SALANT

DEPARTMENT OF PHYSICAL CHEMISTRY, JOHNS HOPKINS UNIVERSITY

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The quantum theory of the heat capacity of solid substances. first developed for monatomic solids by Einstein and by Debye, has been extended to simple inorganic compounds (for example, the alkali halides), by Born and v. Karman and by Nernst.

An attempt will be made in this paper to apply the principles so far developed to the heat capacities of crystalline aliphatic compounds. No effort for a rigorous analysis will be made: the paucity of data and knowledge of these substances does not warrant it.

Born and v. Karman[1] have shown that the molecular heat of a polyatomic crystal is expressed by a combination of Debye and Einstein functions. Thus if we restrict our attention to moderate temperatures, we may write for a crystal whose molecule contains n atoms,

$$C_v = \sum_{j=1}^{3} D'(\nu_j/T) + \sum_{j=4}^{3n} E'(\nu_j/T) \qquad (1)$$

where D' and E' are Debye and Einstein functions, respectively, of a linear oscillator of frequency ν_j.

As the elastic properties of organic substances are not as yet available, and the Debye functions consequently undeterminable, it will be necessary to introduce some approximation. Since, in general, n is large for organic substances, and as the Debye function is usually not greatly different in value from the Einstein at ordinary temperatures, we may write

$$\sum_{j=1}^{3} D' + \sum_{j=4}^{3n} E' = \sum_{j=1}^{3n} E' \qquad (2)$$

and equation (2) will be expected, a priori, to give too low values for C_v at the lower temperatures, this being characteristic of Einstein functions.

Equation (2) is still, however, too ideal for use. Suppose each atom is regarded as vibrating in all directions with a mean frequency $\bar{\nu}_j$, then

$$\sum_{j=1}^{3n} E' = \sum_{j=1}^{n} f(\bar{\nu}_j/T) = C_v \qquad (3)$$

where

$$f(\nu/T) = \frac{3R(\beta\nu/T)^2 \exp(^{\beta\nu/T})}{(\exp_{\beta\nu/T})-1)^2} \quad (4)$$

the Einstein equation for the atomic heat.[2]

If furthermore, each atom of the same kind is regarded as vibrating with the same frequency, regardless of its position in the molecule, then for a compound $C_xH_yO_zN_w$,

$$C_v = Xf(\nu_c/T) + Yf(\nu_H/T) + Zf(\nu_o/T) + Wf(\nu_N/T) \quad (5)$$

Equation (5) is merely the Neumann-Regnault-Kopp law with the atomic heats calculated by the Einstein equation instead of given empirically, and, consequently, allowing for variation of C_v with temperature. It differs from the method for the molecular heat capacity of compounds introduced by Russell[3] in that it uses the Einstein instead of the Nernst-Lindemann equation for the atomic heats.

As the long infra-red regions of organic substances are as yet unmapped, it is necessary to use whatever approximations exist in order to obtain the atomic frequencies. From considerations based on the Lindemann melting-point formula, Koref[4] deduced that, if an atom vibrates with a frequency ν in a solid compound of absolute melting-point T_s and if its frequency in the pure, solid state is ν', then

$$\nu/\nu' = \sqrt{T_s}/\sqrt{T_s'} \quad (6)$$

where T_s' is the melting-point of the pure solid.

This relation (6), can be used, in fact, as it is the only one, it must be used, in order to compare (4) and (5) with measured molecular heats.

The heat capacities of oxalic acid, glycerol and glucose obtained in this way were all much greater than their measured heat capacities (fifty per cent for glucose at room temperatures).[5] There was nothing in either the empirical formulas or the melting-points of these compounds to account for this result; it was natural, therefore, to look to their structural formulae for the cause.

It is not unreasonable to suppose that the principal influence on the vibrations of atoms in organic molecules is their bonding. Now, the other higher melting compounds, urea and formic acid, have no C—C bonds, whereas in oxalic acid, glycerol and glucose, the carbon atoms are bound to each other. It seemed possible that the C—C bond in the higher melting compounds is such as to restrict the vibrations of the carbon atoms so connected to the order of the vibrations of carbon bound to carbon in the pure state, that is, that

$$f(\nu_c/T) = [C] \quad (7)$$

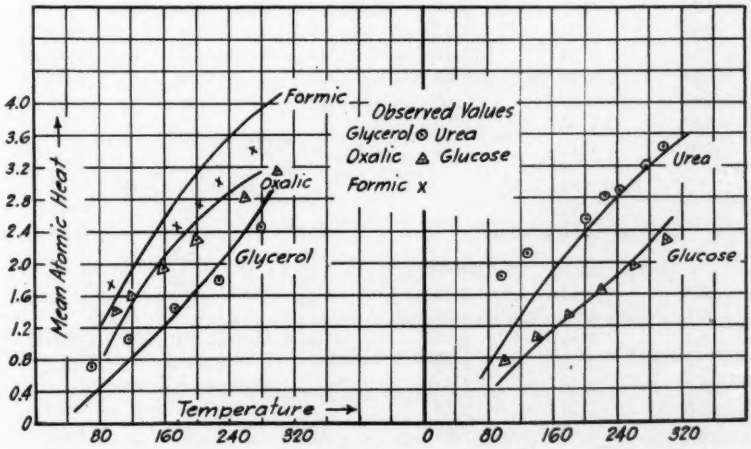
where $[C]$ is the atomic heat of diamond measured at the temperature T. The calculated values of oxalic acid, glycerol and glucose appearing below are based on the assumption of equation (7).

In order to reduce the values to the same scale, the mean atomic heat

$$\overline{C} = C_v/n$$

is calculated below and compared with the mean measured atomic heat $C_p - C_v/n$ being, of course, small. The calculations and comparisons are made for those aliphatic compounds only whose molecular heats may be regarded as reliably measured.

The Einstein equations, $f(\nu/T)$, are evaluated by means of Frl. Miethings's tables in Nernst's monograph.[6] The atomic heats of carbon



are taken from Nernst's measurements tabulated by Miething.[7] When the melting-point of the compound is not given by the worker measuring its heat capacity, the value found in Landolt-Börnstein[8] is used.

The melting-points and densities necessary for the calculation of ν' by the Lindemann melting-point formula[9] are taken from Landolt-Börnstein; the best value for the constant in the equation is, according to Blom[10] 3.1×10^{12} and for β according to Nernst,[6] 4.863×10^{-11}.

The results appear in the following tables. They are self-explanatory. Curves are drawn, from 100°K to room temperature, of the calculated mean atomic heats of those substances melting above 0°C, that is, for formic acid, glycerol, urea, oxalic acid and glucose. All temperatures are absolute and atomic heats are in gram calories per degree.

VALUES OF $\beta\nu'/\sqrt{T_s}$

C	H	O	N
28.65	63.3	16.85	16.89

Formic Acid, HCOOH
T_s: 281.5
$\bar{C}$ per mean g.-atom

T	CALC.	OBS.[11]
270	2.85	3.42
237	3.50	3.02
205	3.11	2.73
176	2.78	2.48
94	1.36	1.73

Oxalic Acid, HOOC.COOH
T_s: 462.6
$\bar{C}$ per mean g.-atom

T	CALC.	OBS.[12]
300	3.34	(3.17)
260	3.04	(2.82)
200	2.50	2.30
160	2.07	1.95
120	1.50	1.60
100	1.12	1.41

Urea, $(NH_2)_2CO$
T_s: 405.8
$\bar{C}$ per mean g.-atom

T °K	CALC.	OBS.[11]
298	3.34	3.44
275	3.13	3.19
244	2.83	2.87
224	2.63	2.83
201	2.36	2.54
128	1.44	2.13
97	0.91	1.83

Glycerol, $CH_2OH.CHOH.CH_2OH$
T_s: 291
$\bar{C}$ per mean g.-atom

T	CALC.	OBS.[13]
280	2.58	2.46
227	1.96	1.79
174	1.36	1.44
116	0.80	1.07
70	0.34	0.72

Glucose, $CH_2OH(CHOH)_4CHO$
T_s: 419
$\bar{C}$ per mean g.-atom

T	CALC.	OBS.[14]
300	2.46	2.29
260	2.04	1.95
220	1.64	1.64
180	1.27	1.34
140	0.95	1.06
100	0.57	0.78

Ethyl Alcohol, $CH_3.CH_2OH$
T_s: 158.7
$\bar{C}$ per mean g.-atom

T	CALC.	OBS.[5]
140	1.77	1.60
120	1.40	1.52
100	1.04	1.29

Methyl Alcohol, CH_3OH
T_s: 176
$\bar{C}$ per mean g.-atom

T	CALC.	OBS.[5]
152	1.92	2.36
112	1.26	1.91
101	1.09	1.77
89	0.87	1.61

n-Butyl Alcohol, $CH_3.(CH_2)_2.CH_2OH$
T_s: 183.9
$\bar{C}$ per mean g.-atom

T	CALC.	OBS.[5]
151	1.72	1.35
145	1.61	1.32
111	1.02	1.11

Acetone, $CH_3.CO.CH_3$
T_s: 178.5
$\bar{C}$ per mean g.-atom

T	CALC.	OBS.[15]
173	2.38	2.32
153	2.07	2.09
133	1.67	1.80

From the curves and tables it is seen that the heat capacities, evaluated by equations (6), (4), (5) and (7) are uniformly too low at the lower temperatures, as anticipated. Above 180°K, however, the calculated differ from the measured values by, on the average, about $\pm 7.5\%$ of the latter, the largest single deviation being 16%, for formic acid at 240°.

Considering the number of approximations required to bring the equations into a form that can be applied, this agreement with measurement is as good as can be expected, especially since the only information about any compound used for the calculation of its molecular heat is its melting-point and its structural formula. The exact derivation of the heat capacities of organic substances from their molecular and atomic properties awaits full knowledge of their elastic behavior and of their infra-red spectra (particularly for long waves), and probably also of their crystal structure.

[1] Born, M., *Atomtheorie d. festen Zustandes.* Teubner, Berlin (1923).
[2] Einstein, A., *Ann. Physik,* **22,** 180 (1907).
[3] Russell, *Physik Zs.,* **13,** 63 (1912).
[4] Koref, F., *Ibid.,* **13,** 183 (1912).
[5] Parks, G. S., *J. Amer. Chem. Soc.,* **47;** 338 (1925).
[6] Nernst, W., *Grundlagen d. neuen warmesatzes,* p. 200. Knapp, Halle, 1924.
[7] Miething, H., *Tabellen zur Berechnung, usw.,* p. 14. Knapp, Halle, 1920.
[8] Landolt-Börnstein, *Phys.-Chem. Tabellen,* Springer, Berlin, 1923.
[9] Lindemann, F. A., *Physik Zs.,* **11,** 609 (1910).
[10] Blom, C. E., *Ann. Physik,* **42,** 1397 (1913).
[11] Gibson, Latimer and Parks, *J. Amer. Chem. Soc.,* **42,** 1533 (1920).
[12] Nernst, W., in Miething, *cit. supra.,* p. 40.
[13] Gibson and Glauque, *J. Amer. Chem. Soc.,* **93,** 45 (1923).
[14] Simon, F., *Ann. Physik,* **68,** 241 (1923).
[15] Maass, O., and Waldbauer, J., *J. Am. Chem. Soc.,* **47,** 1 (1923).

THE DENSITY AND ATOMIC WEIGHT OF HELIUM

BY GREGORY PAUL BAXTER AND HOWARD WARNER STARKWEATHER

T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY

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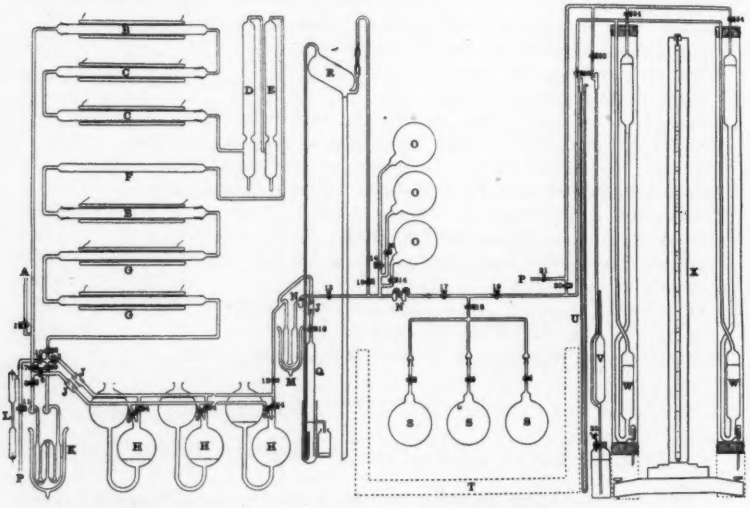
The atomic weight of helium is one of especial interest at present because of the practical identity in mass of the helium atom the α particle of radioactivity and because of certain theories concerning the constitution of heavier atoms. The only known method of finding the atomic weight of helium with accuracy is through the density of the gas. In a recent paper we described certain refinements in the experimental method of determining gas densities as applied to the density of oxygen.[1] We have now extended the work to include helium and present herewith the results obtained up to this time.

Helium of about ninety-five per cent purity was very kindly furnished by the U. S. Navy Department. This gas had been used in the dirigible Shenandoah and repurified. It was first subjected to chemical purification by passing successively over hot copper, hot copper oxide, aqueous potassium hydroxide, solid potassium hydroxide, phosphorus pentox-

ide, hot copper and hot calcium, and was stored in a battery of seven glass-mercury gasometers, so connected that the gas could be recirculated through the purifying train. The apparatus was constructed entirely of glass with ground joints and stopcocks, so that the gas came in contact with nothing else after entering the train.

After the chemical purification had been carried as far as possible the gas was further subjected to physical purification by differential ad-



A	Inlet for helium	*N,N*	Dust traps
B,B	Hot copper	*O,O,O*	Storage reservoirs
C,C	Hot copper oxide	*P,P*	Leads to Gaede mercury pump
D	Aqueous potassium hydroxide	*Q*	Collecting tube from Töpler pump
E	Solid potassium hydroxide	*R*	Töpler pump
F	Resublimed phosphorous pentoxide	*S,S,S*	Density globes
G,G	Hot calcium	*T*	Ice bath for density globes
H,H,H	Three of seven mercury gasometers	*U*	Open arm manometer
J,J,J	Mercury traps	*V*	McLeod gauge
K,M	Chilled chabazite	*W,W*	Barometers
		X	Meter bar

sorption on anhydrous chabazite[2] at low temperatures. The chabazite was contained in a multiple U-tube and was first thoroughly outgassed at 550° in a good vacuum. Then, after immersion of the U-tube in liquid air or liquid nitrogen, the gas was several times circulated over the adsorbent. The volume of the gas was markedly reduced in this process owing to very considerable adsorption of helium as well as the more adsorbable impurities. After the first treatment with adsorbent the adsorbed

gas was collected in a reservoir. Subsequent examination of this gas by re-adsorption on chabazite and slow evaporation of the adsorbed material at gradually increasing temperatures into a spectrum tube which was frequently exhausted, showed successively neon, hydrogen, argon and nitrogen, all in appreciable quantities, with a trace of mercury.

The chabazite was again outgassed at 550° and the fractional adsorption was repeated. The adsorbed gas this time apparently contained only nitrogen besides helium. After three such treatments the spectrum of the purified gas showed only helium with traces of mercury and hydrogen, the latter possibly being due to moisture, since the hydrogen spectrum only appeared some time after the discharge began to pass through the freshly filled tube.

Using the apparatus and method described in the paper on oxygen, the three one-liter globes were filled with helium at 0° and about 760 mm. and were weighed. In filling the globes the gas was passed over the chilled chabazite in the main adsorbing tube and also through a second similar but smaller tube located in the train near the globes. The gas adsorbed by the chabazite still contained a trace of nitrogen and in the first experiment the observed density was very slightly higher than that in any later experiment.

After the gas had been returned to the gasometer by means of a Töpler pump it was again circulated twice over the adsorbent and the globes were filled as before. In this experiment the adsorbed gas contained less nitrogen than in the previous one, and the observed density was very slightly lower than in the first experiment.

Two later sets of density determinations with intermediate circulation of the gas over chilled adsorbent failed to alter the density found in this second experiment.

In correcting the weight of one liter of gas to 0° and 760 mm. in latitude 45° at sea level the following constants have been used:

Density of water at 0°	0.999868
Cubical coefficient of expansion of mercury	0.0001818
Coefficient of expansion of helium[3]	0.003663
Coefficient of deviation from Boyle's Law 0-1 atmosphere[4]	0.00000
Force of gravity at latitude 45° and sea level	980.616
Force of gravity at Coolidge Laboratory	980.376

THE DENSITY OF HELIUM

0° and 760 mm. at Sea Level, Lat. 45°

NUMBER OF EXPERIMENT	NUMBER OF TREATMENTS WITH ADSORBENT	GLOBE I	GLOBE II	GLOBE III	AVERAGE
1	3	0.17853	0.17850	0.17858	0.17854
2	5	0.17840	0.17848	0.17844	0.17844
3	6	0.17844	0.17846	0.17849	0.17846
4	7	0.17849	0.17841	0.17849	0.17846
Average of experiments 2, 3, 4		0.17844	0.17845	0.17847	0.17845

This table includes all the experiments undertaken. In the first experiment, as already explained, beyond question the helium contained a small amount of nitrogen. Therefore it is omitted in computing the average.

Earlier experimental determinations of the density of helium with a claim to a high degree of precision are as follows:

	DENSITY OF HELIUM
Watson[5]	0.17822
Heuse[6]	0.17856
Taylor[7] (recalculated by Guye[8])	0.17832

Using our average value for the density of helium, 0.17845, and that for oxygen recently found by us, 1.42901, and assuming that helium shows no deviation from Boyle's law over the range 0–1 atmosphere, the following table gives values for the atomic weight of helium computed on the basis of various values for $(PV)_0/(PV)_1$ for oxygen:

$(PV)_0/(PV)_1$ (OXYGEN)	LIMITING VALUE OF MOLAL VOLUME IN LITERS	ATOMIC WEIGHT OF HELIUM
1.00085	22.4122	3.9995
1.00090	22.4133	3.9997
1.00095	22.4144	3.9998
1.00100	22.4155	4.0000

The results indicate clearly that, as has been supposed for some time, the atomic weight of helium cannot be far from 4.000. At present we are attempting to increase somewhat the accuracy of our experiments by using two-liter globes, and at the same time to obtain further evidence as to deviations from Boyle's Law of both gases by observations at pressures considerably less than one atmosphere, and by other methods.

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